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Specification as originally filed, with Application for Patent Serial No: 2,246,608, on
September 4, 1998, by **AKHTAR OSMAN** for **Gel Reduction in High CIS-1,4
Polybutadiene Production Process**

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GEL REDUCTION IN HIGH CIS-1,4 POLYBUTADIENE PRODUCTION PROCESS

An essentially linear cis-1,4 polybutadiene having a very low level of gel content is prepared by a process comprising polymerizing 1,3-butadiene in the presence of a cobalt salt-organo aluminum halide-water catalyst system. The polymerization is carried out in the presence as polymerization diluent of a mixture of C_5 - C_6 cyclo alkane and butene-1, a cobalt salt of an organic acid having 6 to 12 carbon atoms in the organic acid, an organo aluminum halide selected from (i) a mixture of (a) an alkyl halide selected from diethyl aluminum chloride and ethyl aluminum sesqui chloride and (b) an organo aluminum or formula $R_3 Al$ wherein R is an alkyl group having 8 to 12 carbon atoms and (ii) an alkyl group having 8 to 12 carbon atoms, a polymerization modifier selected from 1,2-butadiene and 1,3-cyclo octadiene, and water. The water has been mixed with at least a portion of the polymerization diluent such that the water is present in the polymerization diluent as particles having a diameter of equal to or less than about 1 micron.

**GEL REDUCTION IN HIGH CIS-1,4 POLYBUTADIENE PRODUCTION
PROCESS**

FIELD OF THE INVENTION

The present invention relates to an improved process for the production of polybutadiene having a cis-1,4 content and a reduced gel content.

BACKGROUND OF THE INVENTION

Processes for the production of polybutadiene having a high cis-1,4 content, generally known cis-1,4-polybutadiene, are well known. Such processes include the polymerization of 1,3-butadiene in an inert polymerization diluent using as catalyst a mixture of a transition metal salt, such as a cobalt salt, an aluminum alkyl halide or a mixture aluminum alkyl halides and water. During such processes, some gel is produced, such gel being essentially insoluble particles containing cross-linked polybutadiene. The gel is not a desirable component due to the problems it can cause to equipment used for the production of the polymer and due to the problems it can cause relating to the quality of the cis-1,4-polybutadiene.

It is thus desirable to minimize and reduce to the lowest level possible the extent of gel formation during the polymerization process.

DESCRIPTION OF THE PRIOR ART

U.S. Patent 3,094,514 teaches a process for the production of a cis-1,4-polybutadiene, having a cis-1,4-content greater than 90 per cent by; the polymerization

of 1,3-butadiene in a hydrocarbon diluent the presence as catalyst of an anhydrous dihalide diluent cobalt salt, a monoalkyl aluminum, and dialkyl aluminum monohalide. A similar type of process is described in U.S. Patent 3,135,725. U.S. Patent 3,646,001 teaches that cis-1,4-polybutadiene is produced by polymerizing 1,3-butadiene in the presence of cobalt octoate and diethyl aluminum chloride which have been reacted with benzene containing water. U.S. Patent 4,224,426 teaches the polymerization of 1,3-butadiene to produce cis-1,4-polybutadiene in the presence of a cobalt compound, at least one organo-aluminum chloride and water, the polymerization diluent being a mixture of C₅-C₈ cycloalkane, a saturated aliphatic hydrocarbon or an - monoolefin, and an alkyl substituted benzene having 1 to 4 alkyl substituents. U.S. Patent 5,397,851 teaches a process for the production of a cis-1,4-polybutadiene by the polymerization of 1,3-butadiene in an inert hydrocarbon diluent in the presence as catalyst of a diluent cobalt salt, an alkyl aluminum chloride, a tri-alkyl aluminum compound and water.

SUMMARY OF THE INVENTION

An objective of this invention is a process for the production of a high cis-1,4-polybutadiene having a very low level of gel content.

In accordance with the objective, the invention is directed to an improved process for the preparation of an essentially linear cis-1,4-polybutadiene having a very low level of gel content which comprises polymerizing 1,3-butadiene in the presence of a cobalt salt-organo aluminum halide-water catalyst system, the improvement being that the polymerization is carried out

in the presence as polymerization diluent of a mixture of a C_5-C_8 cyclo alkane and butene-1, a cobalt salt of an organic acid having 6 to 12 carbon atoms in the organic acid, an organo aluminum halide selected from (i) a mixture of (a) an alkyl aluminum chloride selected from diethyl aluminum chloride and ethyl aluminum sesquichloride and (b) an organo aluminum of formula R_3Al wherein R is an alkyl group having 8 to 12 carbon atoms and (ii) an alkyl aluminum chloride wherein the alkyl group has 8 to 12 carbon atoms, a polymerization modifier selected from 1,2-butadiene and 1,3-cyclo octadiene, and water, said water having been mixed with at least a portion of said polymerization diluent such that the water is present in said polymerization diluent as particles having a diameter of equal to or less than 1 micron.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, the cobalt salt contains an organic acid having 6 to 12 carbon atoms in the organic acid. Suitable such cobalt salts include but are not limited to cobalt hexanoate, octoate and naphthenate. The organo aluminum halide may be a mixture of diethyl aluminum chloride or ethyl aluminum sequichloride, the ethyl aluminum sesqui chloride being a mixture containing approximately equi molar amounts of diethyl aluminum chloride and ethyl aluminum dichloride, with an organo aluminum R_3Al in which R is an alkyl group having 8 to 12 carbon atoms such as the straight or branched chain and the cyclic aliphatic hydrocarbon groups as illustrated by 2-ethyl hexyl, octyl, decyl, dodecyl and the like. The organo aluminum halide may also be an alkyl aluminum chloride wherein the alkyl group is the same as the alkyl group R herein before

defined. Preferred of the cobalt salts are cobalt octoate and cobalt naphthenate, and of the aluminum compounds are a mixture of diethyl aluminum chloride and one of trioctyl, tridecyl or tridodecyl aluminum, and one of dioctyl, didecyl or didodecyl aluminum chloride.

The polymerization diluent is a mixture of a C₅-C₆ cyclo alkane and butene-1 wherein the cyclo alkane may be selected from cyclopentane and cyclohexane, with cyclohexane being preferred.

In a preferred process, using cyclohexane and butene-1 as the diluent the weight ratio of butene-1 in the cyclohexane-butene-1 mixture may be from about 24 to about 40, preferably from about 24 to about 38 and most preferably from about 34 to about 36, weight per cent. A preferred cobalt salt is cobalt octoate which is used with a preferred aluminum compound which is a mixture of diethyl aluminum chloride and trioctyl aluminum, wherein the molar ratio of cobalt octoate to the total of the diethyl aluminum chloride plus trioctyl aluminum is from about 1:15 to about 1:30, preferably from about 1:15 to about 1:20 and wherein the molar ratio of chlorine in the diethyl aluminum chloride to the total aluminum in the diethyl aluminum chloride plus trioctyl aluminum is from about 0.7:1 to about 0.95:1, preferably from about 0.8:1 to about 0.9:1.

The amount of 1,3-butadiene in the 1,3-butadiene plus diluent mixture may be from about 15 to about 35, preferably from about 25 to about 35, weight percent. The polymerization modifier is selected from 1,2-butadiene and 1,3-cyclooctadiene, with 1,3-cyclooctadiene being preferred. The amount of polymerization modifier may be from about 1.6 to about

3.5, preferably from about 1.95 to about 3.0, millimols per mole of 1,3-butadiene in the polymerization mixture.

~~The polymerization mixture also contains water.~~

The amount of water is from about 0.3 to about 0.8, preferably from about 0.5 to about 0.65, millimols per millimol of the alkyl aluminum chloride used. The water is mixed with at least a portion of the polymerization diluent. Accordingly, the water may be mixed with cycloalkane alone, or, preferably with cycloalkane and butene-1 mixture. The mixing of the water with the polymerization diluent is such that the water as present in the polymerization diluent as particles having a diameter of equal to or less than 1 micron[NOTE: USE METRIC!]. Because of the very low solubility of water in hydrocarbons, including the polymerization diluents, and because of the very, very long time to achieve a solution of water in such hydrocarbons, it is necessary for the present polymerization system to disperse the water in the polymerization diluent as very small particles to provide as high as possible a surface area to weight ratio for the particles so that interaction with the aluminum compound(s) is as efficient as possible, which is believed to be significant in reducing the amount of gel in the polybutadiene produced. The dispersion of water in the polymerization diluent may be achieved by various means such as, but not limited, mechanical methods and sonic treatment. The improvement of the present invention is not dependent on the method used to obtain the dispersion of water in the polymerization diluent and is only dependent on having the water present in the polymerization diluent as particles having a diameter of equal to or less than 1 micron and preferably about 0.5 to about 1 micron.

The polymerization may be undertaken at a temperature of from about -10°C to about 50°C , preferably from about 5°C to about 40°C and most preferably from about 15°C to about 35°C . The polymerization may be carried out in a batch process or in a continuous process, the continuous process being preferred. The reaction time for the polymerization may be from about 20 to about 90 minutes, preferably from about 25 to about 60 minutes. However, the reaction time is not a critical aspect of the process and may be affected by the desired conversion of the 1,3-butadiene to polymer which may range from about 40 to about 90 percent.

The gel content of the polymer is determined by a method in which the gel is separated from a solution of the polymer in styrene and weighed. In detail, approximately 50g of polymer, accurately weighed, is dissolved in pure, filtered styrene to produce an approximately 4 weight percent by volume solution. The polymer-styrene mixture is shaken for 4 to 5 hours, then allowed to stand for 10 minutes and then filtered through a previously weighed filtration screen of 400 mesh. The filtration screen is then weighed again and the amount of wet gel is calculated as parts per million by weight based on the original weight of polymer used. Gel contents of less than about 250 ppm are desirable and less than about 150 ppm are more desirable and less than about 100 ppm are most desirable. In order to provide the greatest accuracy to the gel content of the polymer, normally at least three and up to 5 samples of the polymer are used to provide the corresponding number of gel content measurements.

In the following examples, the 1,3-butadiene was obtained from Union Carbide, the cyclohexane and butene-

1 was Phillips pure grade and all three were passed through a column containing 4A molecular sieves followed by passage through a column containing 13X molecular sieves before use in polymerization. The 1,3-cyclooctadiene was used as a 20 weight percent solution in cyclohexane from Aldrich Chemical Company. Diethyl aluminum chloride in hexane as a 1 molar solution was from Albemarle Corporation and Akzo Nobel. Tri-octyl aluminum in heptane (20% wt.) was obtained from Albemarle Corporation as a 25.3 wt.% solution. Cobalt octoate was obtained from Mooney Chemical Inc. and used as a 6% cobalt solution in cyclohexane. Diethyl aluminum chloride was mixed with tri-octyl aluminum in sealed bottles under an inert gas in such ratios as to provide a solution having an average composition of $\text{Et}_{1.8}\text{Oct}_{0.3}\text{Al}_1\text{Cl}_{0.9}$ in cyclohexane which was used in all examples and is referred to as M-DEAC. Polymerization was undertaken in sealed 1 litre polymerization bottles at a temperature of 27°C for 40 minutes at the end of which time the polymerization was stopped by the injection of 5 ml of ethanol containing required amount of stabilizer and the polymer was recovered by steam coagulation.

The following examples illustrate the invention and are not intended to limit the scope of the invention.

EXAMPLE 1

Using 1 liter glass bottles capped with gasketted crown caps, 110 g of cyclohexane, 80 g of 1,3-butadiene, 60g of butene-1, 1.8 ml of a 20% solution of 1,3-octadiene in cyclohexane, 0.01 ml of pure distilled water, 0.54 ml of a 25% solution of M-DEAC and 0.19 ml of a 0.25% solution of cobalt octoate in cyclohexane

were charged the glass bottles. When the cobalt octoate was added, the glass bottles were placed in an agitated polymerization bath maintained at 27°C for 40 minutes, followed by addition of ethanol to stop polymerization. The polymer was recovered and dried and samples used to measure the gel content, with the results shown in Table 1. Experiment #1 is a control in which the cyclohexane plus water was shaken for 5 minutes which produced clearly visible particles of water in the cyclohexane. The other components were added after the shaking. In Experiment #2, the cyclohexane and water was subjected to sonification for 5 minutes in a Branson ultrasonic cleaner which produced a mixture of water particles in cyclohexane in which the water particles had a mean diameter of about 0.2 micron. The other components were added after completion of the ultrasonic mixing. For Experiment #3, the cyclohexane, 1,3-butadiene, butene-1 and water were subjected to sonification as herein before, the water particles having a mean diameter of between 0.2 and 0.5 micron. The other components were added on completion of the ultrasonic mixing. In Experiment #4, the cyclohexane, 1,3-butadiene, butene-1 and water were subjected to shaking for 48 hours producing water particles having a mean diameter of between 0.5 and 1 micron. The other components were added on completion of the shaking. The gel data provided in Table 1 clearly show that the presence of water particles having a diameter of equal to or less than 1 micron resulted in the production of polymers having significantly reduced gel contents.

EXAMPLE 2

Using the procedure and components described in Example 1, polymerizations were undertaken in which the

cyclohexa 1,3-butadiene, butene-1 wa and M-DEAC were mixed by shaking for times ranging from 0 up to 30 minutes. The other components were added on completion of the shaking. The gel results shown in Table 2 show that when the water particle size is reduced to or

TABLE 1

Experiment #	1	2	3	4
Gel ppm	1200	15	80	95
	1540	28	56	82
	1010	32	110	100
	1610	26	75	73
		30	100	
Average Gel ppm	1340	26	84	87

TABLE 2

Shaking Time Minutes	Water Particles Size Microns	Gel PPM
0		2950
5		1680
10		863
15		520
20		120
25	about 0.5 to about 1.0	50
30	about 0.5 to about 1.0	38

less than 1 micron, the gel content of the polymer is significantly reduced.

EXAMPLE 3

Using the procedure described in Example 1, the following experiments were undertaken. 110 g of cyclohexane and 0.011 ml of water was subjected to sonification for 5 minutes producing a mixture containing particles of water having a mean diameter of about 0.5 microns. Following this, 80g of 1,3-butadiene, 2.0 ml of a 20% solution of 1:3 cyclooctadiene in cyclohexane, 60g of butene-1, 1.25 ml of a 12% solution of diethyl aluminum chloride in cyclohexane and 0.2 ml of a 0.25% solution of cobalt octoate in cyclohexane were added and the contents immersed in an agitated water bath at 27°C for 40 minutes. After stopping the polymerization, the polymer was recovered and the gel content was determined to be 120 ppm. In a control experiment, the same procedure was followed except that instead of being sonified, the cyclohexane and water was mixed by shaking. The water particles were found to have a mean diameter of about 10 u. The resulting polymer was found to have a gel content of greater than 3000 ppm.

What is claimed is:

1. An improved process for the preparation of an essentially linear cis-1,4-polybutadiene having a very low level of gel content which comprises polymerizing 1,3 butadiene in the presence of a cobalt salt-organo aluminum halide-water catalyst system, the improvement being that the polymerization is carried out in the presence as polymerization diluent of a mixture of a C₅-C₆ cycloalkane and butene-1, a cobalt salt of an organic acid having 6 to 12 carbon atoms in the organic acid, an organo aluminum halide selected from (I) a mixture of (a) an alkyl aluminum chloride selected from diethyl aluminum chloride and ethyl aluminum sesquichloride and (b) an organo aluminum of formula R₃Al wherein R is an alkyl group having 8 to 12 carbon atoms and (ii) an alkyl aluminum chloride wherein the alkyl group has 8 to 12 carbon atoms, a polymerization modifier selected from 1,2-butadiene and 1,3-cyclooctadiene, and water, said water having been mixed with at least a portion of said polymerization diluent such that the water is present in said polymerization diluent as particles having a diameter of equal to or less than 0.5.
2. The process of Claim 1 wherein the cycloalkane is cyclohexane.
3. The process of claim 2 wherein the organo aluminum halide is a mixture of diethyl aluminum chloride and an organo aluminum R₃Al.
4. The process of claim 1 or 2 wherein the organo aluminum R₃Al is present in an amount of 0 to 1 percent by weight of the mixture.

5. The process of Claim 4 wherein the organo aluminum is tri-octyl aluminum.
6. The process of Claim 5 wherein the cobalt salt is cobalt octoate.
7. The process of Claim 6 wherein the molar ratio of cobalt octoate to the total of diethyl aluminum chloride plus tri-octyl aluminum is from about 1:15 to about 1:30.
8. The process of Claim ⁷ wherein the molar ratio of chlorine in diethyl aluminum chloride to the total aluminum in diethyl aluminum chloride plus tri-octyl aluminum is from about 0.7:1 to about 0.95:1.
9. The process of Claim 6 wherein the water is mixed with the polymerization diluent by mechanical methods.
10. The process of Claim 6 wherein the water is mixed with the polymerization diluent by sonic treatment.
11. The process of Claim 6 wherein the polymerization temperature is from about 5° to about 40°C.

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54 **Process for the preparation of aluminoxanes.**

57 **Process for preparing aluminoxanes from tri-
kylaluminium compounds and an ultrasonically pro-
duced water dispersion.**

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D,A	US-A-3 300 458 (R.M. MANYIK et al.) * Whole document * ---	1	C 07 F 5/06
A	US-A-3 242 099 (R.M. MANYIK et al.) * Whole document * ---	1	
A	GB-A-1 176 692 (UNION CARBIDE) * Whole document * ---	1	
A	PATENT ABSTRACTS OF JAPAN, vol. 6, no. 266 (C-142)[1144], 25th December 1982; & JP-A-57 158 792 (SUMITOMO KAGAKU KOGYO K.K.) 30-09-1982 * Abstract * -----	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 07 F C 08 G C 08 F
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CATEGORY OF CITED DOCUMENTS			
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